<Division of Materials Chemistry>Polymer Controlled Synthesis

Division of Materials Chemistry
– Polymer Controlled Synthesis –

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BALL, Melissa Lynne (Ph D) Colombia University, U.S.A., 19 November–18 December

Scope of Research

Our research focuses on creation of new organic molecules with potential as key reagents and materials for future science and technologies. Furthermore, we have been developing new organic and polymeric materials based on our tailor-made molecules. For example, we are developing a new living radical polymerization method using heavier heteroatom compounds as controlling agents. Another topic is the synthesis of cycloparaphenylenes, hoop-shaped π-conjugated molecules, based on new synthetic strategies. We also study various condensed states of polymers by both static and dynamic methods to understand the relationship between structure and physical properties.

KEYWORDS

Organic Synthesis
Polymer Synthesis
Living Radical Polymerization
Polymer Properties
Curved π-Conjugated Molecules

Selected Publications

Fan, W.; Tosaka, M.; Yamago, S.; Cunningham, M. F., Living Ab Initio Emulsion Polymerization of Methyl Methacrylate in Water Using a Water Soluble Organotellurium Chain Transfer Agent under Thermal and Photochemical Conditions, *Angew. Chem. Int. Ed.*, **57,** 962-966 (2018).

Kayahara, E.; Hayashi, T.; Takeuchi, K.; Ozawa, F.; Ashida, K.; Ogoshi, S.; Yamago, S., Strain-Induced Double Carbon-Carbon Bond Activations of Cycloparaphenylenes (CPPs) by a Platinum Complex and Its Application for the Synthesis of Cyclic Diketones, *Angew. Chem. Int. Ed.*, **57,** 11418-11421 (2018).

Synthesis of Structurally Controlled Hyperbranched Polymers Using a Monomer Having Hierarchical Reactivity

Hyperbranched polymers (HBPs) have attracted significant attention because of their characteristic topological structure associated with their unique physical properties compared with those of the corresponding linear polymers. Dendrimers are the most structurally controlled HBPs. However, the necessity of a stepwise synthesis have significantly limited their applications in materials science. Several methods have been developed to synthesize HBPs by a one-step procedure, as exemplified by the use of AB_2 monomers and AB' inimers under condensation and self-condensing vinyl polymerization conditions. However, none of these methods provides structurally controlled HBPs over the three-dimensional (3D) structure, i.e., molecular weight, dispersity, number of branching points, branching density, and chain-end functionalities, except under special conditions. We introduced a monomer design concept involving two functional groups with hierarchical reactivity and demonstrated the controlled synthesis of dendritic HBPs over the 3D structure by the copolymerization of the designed monomer and acrylates under living radical polymerization conditions.

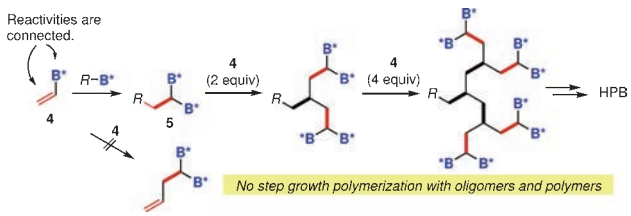

Figure 1. Scheme for the synthesis of structurally controlled hyperbranched polymer.

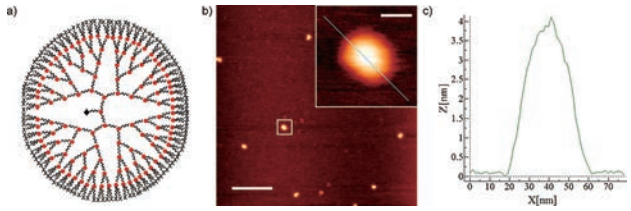

Figure 2. Structure and AFM image of the dendritic hyperbranched polymer.

Strain-Induced Double Carbon–Carbon Bond Activations of Cycloparaphenylenes by a Platinum Complex: Application to the Synthesis of Cyclic Diketones

The carbon–carbon (C−C) bond activation of [n]cycloparaphenylenes ([n]CPPs) by a transition-metal complex was achieved. The Pt^0 complex $Pt(PPh_3)_4$ regioselectively cleaves two C−C σ bonds of [5]CPP and [6]CPP to give cyclic dinuclear platinum complexes in high yields. Theoretical calculations revealed that the relief of ring strain drives the reaction. The cyclic complex was further transformed into a cyclic diketone by using a CO insertion reaction. The mechanism of the formation of the dinuclear platinum(0) complexes was elucidated with DFT calculations, which suggested a stepwise pathway. Both steps of forming the mononuclear platinum complex and the cyclic dinuclear complex were found to be highly exothermic and have low activation energies. The DFT studies also explained regioselectivity of the reaction. The activation of the more strained [5]CPP was significantly faster compared with that of less strained [6]CPP. Consistent with the proposed strain-induced process, larger CPPs, such as [7]CPP and [8]CPP, did not show reactivity.

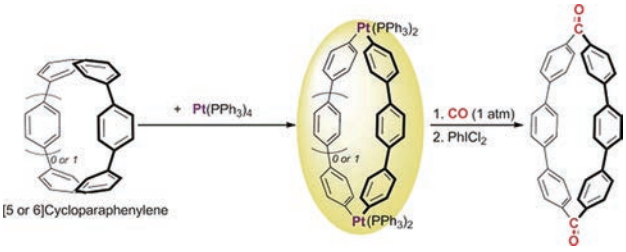

Figure 3. Carbon–Carbon Bond Activations of Cycloparaphenylenes by a Platinum Complex.